

Effect of non-magnetic impurities on the magnetic states of anatase TiO_2

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Abstract. The electronic and magnetic properties of TiO_2 , $\text{TiO}_{1.75}$, $\text{TiO}_{1.75}\text{N}_{0.25}$, and $\text{TiO}_{1.75}\text{F}_{0.25}$ compounds have been studied by using *ab initio* electronic structure calculations. TiO_2 is found to evolve from a wide-band-gap semiconductor to a narrow-band-gap semiconductor to a half-metallic state and finally to a metallic state with oxygen vacancy, N-doping and F-doping, respectively. Present work clearly shows the robust magnetic ground state for N- and F-doped TiO_2 . The N-doping gives rise to magnetic moment of $\sim 0.4 \mu_B$ at N-site and $\sim 0.1 \mu_B$ each at two neighboring O-sites, whereas F-doping creates a magnetic moment of $\sim 0.3 \mu_B$ at the nearest Ti atom. Here we also discuss the possible cause of the observed magnetic states in terms of the spatial electronic charge distribution of Ti, N and F atoms responsible for bond formation.

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1. Introduction

In recent years the scientific world is fascinated by the occurrence of magnetism in non-magnetic materials where unpaired d and/or f electrons are absent. For example, materials like Si[1], pyrolytic graphite, [2] fullerene, [3] CaO, [4, 5] CaB_6 , [6, 7, 8] SiC, [9] *etc.* contain only s and p electrons and are reported to exhibit magnetism. In the case of Si, magnetism is shown to arise from surfaces [1] whereas the observed room temperature ferromagnetism (FM) in the pyrolytic graphite is attributed to the two-dimensional networks of point defects.[2] The origin of FM observed in CaB_6 has been a matter of controversy and two schools of thought exist. One believes that it is arising from magnetic impurities, whereas other has opinion that defects are responsible for the FM.[8] Similarly, defects are also found to be responsible for the creation of magnetic moments in CaO and SiC compounds.[5, 10] Thus the creation of finite magnetic moments in these systems are attributed to the uncompensated spins due to the surface effect, defects, and even to magnetic impurities. In spite of these ambiguities, the phenomenon has not only provided a new dimension to the spintronic based materials but also throws a challenge to appreciate such an occurrence from fundamental physics point of view as knowing the exact cause for the creation of net magnetic moments and the nature of interaction among them are non-trivial.

In this work we have attempted to explore the presence of magnetism in the well studied non-magnetic semiconducting oxide TiO_2 by creating oxygen vacancy and doping non-magnetic elements at oxygen sites. In order to appreciate such an attempt, it is important to note that getting ferromagnetic (FM) state in a non-magnetic semiconductor by means of doping magnetic impurity has attracted a great deal of attention in recent years and has emerged as one of the important branch in the condensed matter physics and materials science.[11, 12, 13, 14, 15, 16] However, the origin of ferromagnetism in such diluted magnetic oxide semiconductors (DMOS) has been controversial, where the possibility of the formation of secondary phase or clusters of magnetic impurity cannot be ruled out. Recently a few reports have appeared which emphasize induction of FM state in non-magnetic semiconducting oxides by means of doping non-magnetic elements, creating defects or changing oxygen stoichiometry.[17, 18, 19, 20, 21, 22] Such DMOS will indeed be quite advantageous, since then one does not need to bother about issues related to incorporation of magnetic impurity in the host matrix or its interaction with the carriers. Study of these doped and undoped oxide semiconductors put forward a hope to manipulate the opto-electronic devices by controlling their magnetic properties. Thus our present attempt is expected to provide some understanding towards the origin of magnetic moment in an otherwise non-magnetic system and its possible applications in the spintronics field.

TiO_2 is chosen for the study due to its well documented wide range of optical, electrical and catalytic applications. TiO_2 based system also possesses good optical transmission in the visible and near infra red regions making it a suitable candidate for the magneto-optic device as well. For the present study we consider three cases: (i)

create oxygen vacancy ($\text{TiO}_{1.75}$), (ii) dope nitrogen ($\text{TiO}_{1.75}\text{N}_{0.25}$), and (iii) dope fluorine ($\text{TiO}_{1.75}\text{F}_{0.25}$) and examine their magnetic states. We take these cases to compare the effect of non-magnetic anion doping of F and N atoms with the aim to evaluate the influence of electron or hole doping on the electronic and magnetic properties of the system. Our results show that the oxygen vacancy does not induce any appreciable magnetization in TiO_2 . However, doping of N and F atoms induces magnetic ground state, with magnetic moments appearing prominently at N and Ti sites, respectively.

2. Computational details

The spin-unpolarized *i.e.* non-magnetic (NM) and spin-polarized (SP) electronic structure calculations of TiO_2 , $\text{TiO}_{1.75}$, $\text{TiO}_{1.75}\text{N}_{0.25}$, and $\text{TiO}_{1.75}\text{F}_{0.25}$ compounds have been carried out by using *state-of-the-art* full-potential linearized augmented plane wave (FP-LAPW) method.[23] The lattice parameters used in the calculations are $a = 3.785$ Å and $c = 9.514$ Å; and the atomic position taken for the oxygen atom is $z = 0.2066$. The muffin-tin sphere radii are chosen to be 2, 1.6, 1.5, and 1.45 a.u. for Ti, O, F, and N atoms, respectively. For the exchange correlation functional, we have adopted recently developed generalized gradient approximation (GGA) form of Perdew *et al.*[24] The self-consistency was achieved by demanding the convergence of the total energy to be smaller than 10^{-4} Hartree/cell. The total magnitude of the force per unit cell comes out to be less than 0.003 Hartree/Bohr.

3. Results and discussions

The anatase TiO_2 crystalizes in body center tetragonal structure (space group $I4_1/amd$) where Ti and O occupy $4a$ (0,0,0) and $8e$ (0,0, z) Wyckoff positions, respectively. Therefore, the conventional unit cell contains 4 Ti and 8 O atoms. The atomic arrangement in the unit cell is shown in Fig. 1. Each Ti atom is surrounded by 6 O atoms. Out of 6 Ti-O bonds, 4 bonds are of equal length (1.937 Å) and rest two have bondlength of 1.965 Å. In order to see the effect of non-magnetic electron and hole doping on the electronic and magnetic properties of the compound we have replaced O2 by fluorine and nitrogen atoms, respectively. Similarly, the effect of oxygen vacancy is also studied by removing O2 atom.

The total density of states (TDOS) per formula unit (fu) of TiO_2 , $\text{TiO}_{1.75}$, $\text{TiO}_{1.75}\text{N}_{0.25}$, and $\text{TiO}_{1.75}\text{F}_{0.25}$ compounds are shown in Fig. 2. The TDOS of TiO_2 in both the spin channels are perfectly symmetric which is in accordance with the non-magnetic ground state of the compound. The band gap of TiO_2 is found to be ~ 2.1 eV, which is about 1 eV lower than experimentally observed value.[11] The discrepancy between the calculated and experimental results is not surprising as GGA calculations are often found to underestimate the band gap of semiconductors and insulators. The creation of oxygen vacancy does not have much influence on the magnetic state of the system as TDOS of $\text{TiO}_{1.75}$ in both the spin channels also look symmetric as evident

from Fig. 2(b). This observation is in contrast to the previous pseudo-potential based calculations showing magnetic ground state driven by oxygen vacancy.[20] The GGA+ U results of Yang *et al.* show the formation of magnetic moment of $1 \mu_B$ each at two neighbouring Ti sites.[20] In order to look into the possibility that on-site Coulomb interaction (U) among Ti $3d$ electrons might be responsible for the creation of magnetic moments in the work of Yang *et al.*, we have also carried out GGA+ U calculation and could not find any magnetic moment at the Ti sites even for $U=4$ eV which is a reasonable value of U for the $3d$ electrons.[25, 26, 27] At this juncture, it is important to note that full-potential calculations are often found to provide more accurate results in comparison to pseudo-potential ones. Our calculations give negligibly small magnetic moment at Ti sites, which is consistent with earlier full-potential based result.[19] Interestingly, oxygen vacancy creates an electron-like band just below the bottom of the conduction band (CB). The band gap between top of the valance band (VB) and bottom of the impurity band is found to be ~ 1.1 eV and that between top of the impurity band and bottom of the conduction band is ~ 0.1 eV. This result suggests that the oxygen vacancy gives rise to significantly large increment in the number of charge carriers at room temperature, which is consistent with the available experimental data.[11]

The doping of non-magnetic impurities at O2 site provides highly asymmetric energy distribution of the states closer to the Fermi level (ϵ_F) in both the spin channels as evident from Figs. 1(c) and 1(d). This suggests the creation of net magnetic moments in the compounds. The ground state of N-doped TiO_2 is found to be magnetic as the energy of SP solution is ~ 102 meV/fu less than that of NM solution. The N-doping shifts the edge of the valence band towards ϵ_F by ~ 0.5 eV. Moreover, it gives rise to extended VB states. As expected N-doping provides hole-like impurity band. Interestingly, the ground state of N-doped TiO_2 is found to be half-metallic as there is no density of states (DOS) at the ϵ_F in the up-spin channel and the band gap in this channel is found to be ~ 2 eV. The F-doping also gives rise to magnetic ground state as the energy of SP solution is ~ 71 meV/fu less than that of NM solution. The VB of F-doped TiO_2 is extended over a wide energy range with the appearance of new states between -10.9 and -8.8 eV which were absent in earlier cases. These states are expected to arise from the fluorine atoms, which becomes clear in later part of the manuscript. As opposed to the case of oxygen vacancy, the electron-like impurity band of F-doped TiO_2 is found to overlap with the CB minimum resulting in metallic ground state as evident from Fig. 1(d). Thus our results provide the simple but elegant way of controlling the electronic transport of TiO_2 as it evolves from a wide-band-gap semiconductor to a narrow-band-gap semiconductor to a half-metallic state and finally to a metallic state with oxygen vacancy, N-doping and F-doping, respectively.

In order to know the energy distribution of different states we have plotted the Ti $3d$ and O $2p$ partial density of states (PDOS) of TiO_2 and $\text{TiO}_{1.75}$ in Fig. 3. It is evident from the Fig. 3(a) that the states closer to the top of the VB have dominating contribution from O $2p$ orbitals, whereas states in the vicinity of the bottom of VB has mixed Ti $3d$ and O $2p$ character. The bottom of the CB consists of Ti $3d$ states.

Moreover, one can see the finite O $2p$ PDOS in the CB region above 2 eV. The finite contribution of Ti $3d$ and O $2p$ orbitals in the VB and CB, respectively suggests the breakdown of the pure ionic model for Ti-O bonds and can be considered as a signature of strong hybridization between Ti $3d$ and O $2p$ states. The effect of oxygen vacancy on the electronic states of TiO_2 is displayed in Fig. 3(b) where we have plotted Ti $3d$ PDOS of Ti1 and Ti2 atoms which have got most influenced by removal of O2 atom. Two obvious features are visible: (i) the bottom of the VB corresponds to Ti2 $3d$ states which shifts by ~ 0.12 eV deeper in comparison to Ti1 $3d$ states and (ii) the contribution of Ti2 $3d$ states to the impurity band is about 75%. The first one may be attributed to the more hybridization of Ti2 $3d$ and O2 $2p$ orbitals in comparison to Ti1 $3d$ and O2 $2p$ orbitals, as the bondlength of Ti2-O2 is ~ 0.03 Å lesser than that of Ti2-O1, resulting in increased separation between bonding and antibonding molecular orbitals. The second one can be attributed to the orbital polarization. In octahedral symmetry two d electrons of the elemental Ti is expected to occupy t_{2g} orbitals. In the anatase structure shown in Fig. 1, only d_{xy} orbital is expected to show significant overlap with O2 $2p$ orbital, resulting in transfer of electron to O2 and making it negatively charged. In the case of vacancy at O2 site, this transferred electron would be taken back by Ti2 and would mainly contribute to the impurity band as seen from the calculation.

The N-doping at O2 site does not have any influence on the magnetic state of Ti atoms. The $2p$ PDOS of N, O1 and O3 are shown in Fig. 4(a) as these states are found to be most influenced by the doping. The distribution of these states is highly asymmetric in both the spin channels suggesting of net magnetic moments at N, O1 and O3 atoms. The magnetic moment at N site is found to be $\sim 0.4 \mu_B$ and that at O1 and O3 sites are $\sim 0.1 \mu_B$ each. The contribution of magnetic moments from rest of the sites is negligibly small. The total magnetic moment per formula unit comes out to be $\sim 0.25 \mu_B$. The distribution of impurity PDOS around the ϵ_F provides valuable information about the nature of magnetic interaction among the magnetic moments of the impurity atoms.[28] In the up-spin channel one can see the absence of states closer to the ϵ_F . However, in the down-spin channel there are finite states in the vicinity of ϵ_F . These states are of highly mixed N $2p$ and O $2p$ characters. One can also see the appearance of a sharp peak just above the ϵ_F which has dominating contribution from N $2p$ orbitals.

Contrary to the N-doping, the F-doping at O2 site gives rise to net magnetic moment of $\sim 0.3 \mu_B$ for Ti2 atom keeping magnetic moments of rest of the atoms negligibly small. The total magnetic moment per formula unit comes out to be $\sim 0.11 \mu_B/\text{fu}$. In Fig. 4(b) we have shown the Ti2 $3d$, O1 $2p$ and F $2p$ PDOS as these states are found to be most influenced by the F-doping. Interestingly, the electron type impurity band has mainly Ti2 $3d$ character. The energy distribution of this band in both the spin channels is highly asymmetric and responsible for creation of magnetic moment at Ti2 site. The states found below -8.8 eV are mainly arising from F $2p$ orbitals and O1 $2p$ orbitals are mainly contributing between -7.8 to -2.9 eV.

The above results clearly establish the magnetic ground state on doping non-

magnetic impurities at the O sites. However, N-doping creates magnetic moments at N site whereas F-doping gives rise to magnetic moment at Ti2 site. Entirely different effect of N- and F- doping at the magnetic moments is unusual and appears to be related with the spatial electronic charge distribution of Ti2, N and F atoms responsible for bond formation. Pure TiO_2 is non-magnetic as the valance electrons are equally populated in both the spin channels. The F $2p$ orbitals are highly localized as evident from Fig. 4(b). Such localization of p orbitals prohibits sharing of electrons from the neighboring Ti2 $3d$ electrons and making transfer of $3d$ electrons to F site energetically more favorable. The F $2p$ orbitals are more than half-filled and hence only down-spin electrons are allowed to be transferred resulting in net spin polarization of Ti2 $3d$ electrons. Contrary to the F $2p$ orbitals, N $2p$ orbitals are extended which can easily share its electrons with neighboring Ti2 $3d$ orbitals making Ti2-N bonds more covalent in nature. In covalent bond there are equal probability of sharing the up- and down-spin electrons. Moreover, N $2p$ orbitals contains one more electron in comparison to Ti2 $3d$ electrons. Thus the sharing of Ti2 $3d$ and N $2p$ electrons is expected to provide net spin polarization at N site due to inert $2p$ electron.

Finally, we explore the possibility of utilization of the above results in the real systems. First hindrance appears to be the synthesis of such compounds as the dopant percentage (either N or F) studied here is quite high if we compare with the results of ZnO .^[5] However, Chen *et al.* have reported to synthesize as high as 15% N-doped TiO_2 .^[29] Since the difference between ionic radius of O and N ions is almost the same as that between O and F ions, therefore, F-doped compound is also expected to be synthesized easily. Moreover, we performed calculations on 6.125% N- and F- doped TiO_2 and found similar results as far as formation of magnetic moments are concerned. Thus it appears that the synthesis of compounds which shows finite magnetic moments is not a problem. However, the mere formation of finite magnetic moments at different sites does not guarantee the collective magnetism which is essential for any practical application. To ascertain this one needs to estimate the optimal concentration of dopant required for percolation of the magnetic interaction. Any such attempt with fair accuracy is very much time consuming under FP-LAPW method and beyond the scope of the present work. However, we feel that the dopant percentage studied here is high enough to induced collective magnetism and motivate other workers to look into this aspect.

4. Conclusions

In conclusion, we have examined the effect of oxygen vacancy and doping of non-magnetic anion in TiO_2 on its magnetic properties. It turns out that oxygen vacancy leads to electron doping in the system, though it does not induce appreciable magnetic moment in the system. Interestingly, doping of N gives rise to robust ferromagnetic half-metallic ground state for $\text{TiO}_{1.75}\text{N}_{0.25}$ with the appearance of magnetic moment at N and two neighboring O sites and hence expected to provide an innovative prospect

for a novel class of DMOS material with anion doping. On the other hand the ground state of F-doped sample is found to be metallic with the induction of magnetic moment at Ti site nearest to F atom. Since we observe that the electronic state of TiO_2 can be controlled from wide-band-gap semiconductor to narrow-band-gap semiconductor to half metallic to metallic states by selectively managing the anion site, it gives us a hope to tune the band gap of TiO_2 to further extend its application domain in photo-catalytic and magneto-optic devices. Such a study would also provide us an understanding of the origin of magnetism in a semiconducting oxide system by non-magnetic anion doping.

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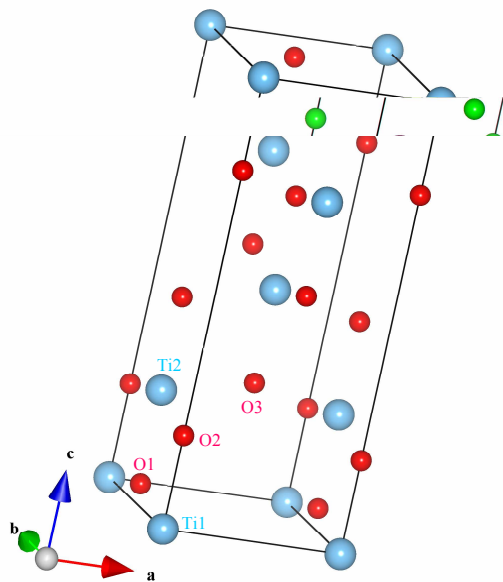


Figure 1. (Color online) Atomic arrangements of TiO_2 in the unit cell.

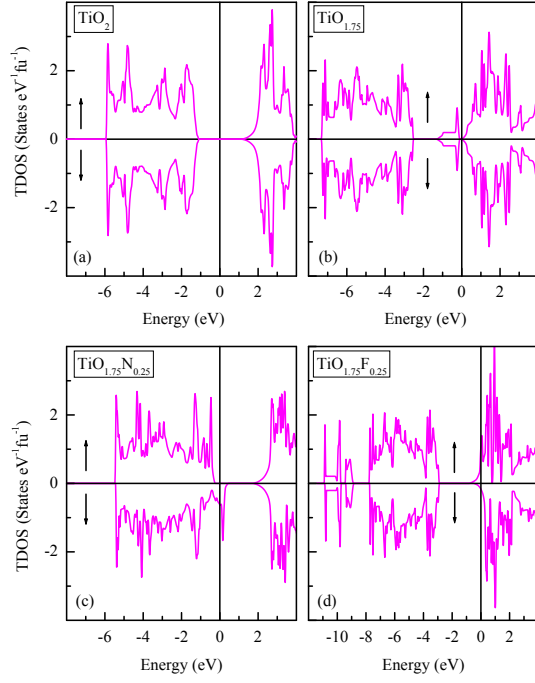


Figure 2. (Color online) Total density of states (TDOS) per formula unit of (a) TiO_2 , (b) $\text{TiO}_{1.75}$, (c) $\text{TiO}_{1.75}\text{N}_{0.25}$, and (d) $\text{TiO}_{1.75}\text{F}_{0.25}$ compounds.

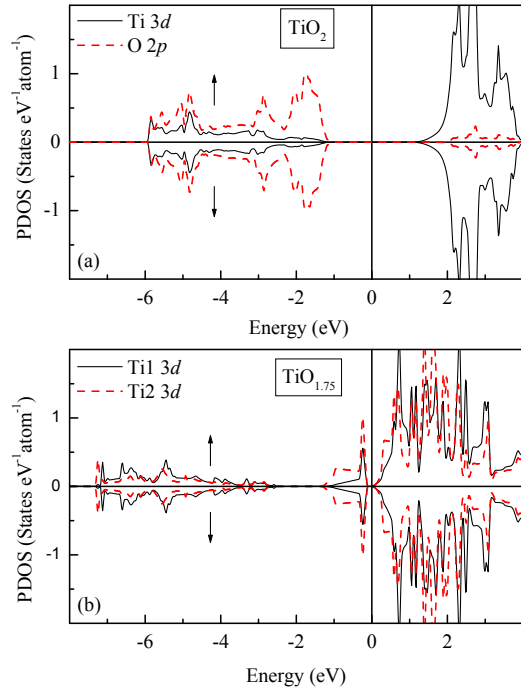


Figure 3. (Color online) Partial density of states (PDOS) of (a) Ti 3d and O 2p states in TiO_2 and (b) Ti1 3d and Ti2 3d states in $\text{TiO}_{1.75}$.

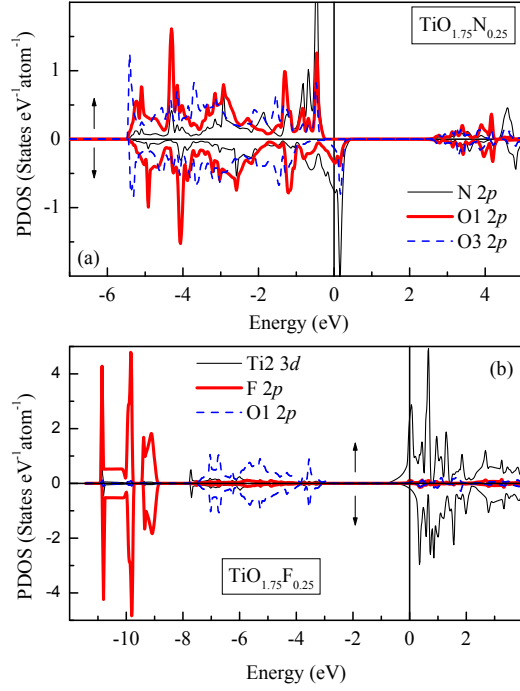


Figure 4. (Color online) Partial density of states (PDOS) of (a) N 2p, O1 2p and O3 2p states in $\text{TiO}_{1.75}\text{N}_{0.25}$ and (b) Ti2 3d, F 2p and O1 2p states in $\text{TiO}_{1.75}\text{F}_{0.25}$.